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14. ABSTRACT
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pCO$_2$ and CO$_2$ exchange during high bora winds in the Northern Adriatic

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ABSTRACT

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1. Introduction

Previous studies have suggested that episodic high wind events have a potential for influencing surface water pCO$_2$ and air–sea CO_2 exchange (Bates 2007; Bates et al., 1998; Edson et al., 2011; Hood et al., 2001). These studies have mostly been performed in the open ocean and have reported an enhancement in air–sea flux due to high transfer velocity (k) and increase of surface water pCO$_2$ caused by upward mixing of water relatively enriched in CO_2, and/or movement of water masses with different properties through the system. A very limited set of observations is currently available on the biogeochemical response to high wind events, such as bora in coastal areas and their subsequent role in air–sea CO_2 exchange.

The pCO$_2$ of surface seawater is controlled by thermodynamic changes, air–sea exchange, biological activity, vertical mixing, and horizontal advection. Temperature increases lead to higher pCO$_2$ and biological production to lower pCO$_2$, while gas exchange reduces (increases) water pCO$_2$ when water concentration is higher (lower) than atmospheric CO_2. Vertical mixing and horizontal advection from areas where wind strength, stratification and water pCO$_2$ may be different could play particularly important roles in a coastal environment due to the shallow depths and small horizontal spatial scale of variation respectively. For example, during high wind events, bottom water with higher pCO$_2$ can suddenly mix with surface water that has lower pCO$_2$ increasing surface and decreasing bottom pCO$_2$. In ocean CO_2 sink conditions (i.e. the ocean undersaturated with respect to atmospheric CO_2), this increase in surface pCO$_2$ can have a negative feedback by decreasing the amount of ocean pCO$_2$ undersaturation faster than would happen by gas exchange alone.

Bora is a cold katabatic wind prevailing from a northeasterly direction and is the most common wind in the Northern Adriatic. Bora forms thin sea surface wind jets that are spatially influenced by the local topography and are characterized by a sudden startup and a short duration (order of one to a few days in the summers and six to fourteen days in the winter), with mean speeds over 15 m s^{-1} and with gusts greater than 30 m s^{-1} (Stravisi, 2001). Bora winds normally occur more than 40 days per year. Bora is most common in autumn and winter, but can also be present during the summer period. The strength, mean positions and extension of bora jets vary considerably between different events (Pullen et al., 2007) and therefore the response of the system cannot be determined based on a single bora episode.

It has been well established that bora has a strong effect on the physical environment of the Northern Adriatic, such as its circulation, stratification, and heat and momentum fluxes (Dorman et al., 2006; Jeffries and Lee, 2007; Kuzmić et al., 2006; Malačič and Petelin,

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2006; Pullen et al., 2007; Signell et al., 2010). It generates a wind-induced "double gyre" circulation, with a cyclonic gyre in the northern part of the basin and an anticyclonic gyre in front of the Southern Istrian coast (Kuzmić and Orlić, 1987; Kuzmić et al., 2006). In the Gulf of Trieste (GOT), the most northern semi-enclosed basin in the Northern Adriatic (Fig. 1), Malačič and Petelin (2009) show a generally cyclonic circulation in the deeper layer in all seasons with an inflow into the GOT which is enhanced during spring time. Tidal currents can exceed 20 cm s^{-1} in the GOT and are particularly enhanced along the Croatian/Slovenian coast at the southern entrance to the gulf (see Fig. 7 of Malačič et al., 2000). At the surface, the circulation of the gulf is predominantly anticyclonic during the stratified season due to the inertial plume of the Isonzo River, and there is an outflow from the gulf (Malačič and Petelin, 2009; Zavatarelli and Pinardi, 2003). During the intense bora episodes in the winter, studies have suggested that bora winds drive flow downwind at the surface, forming an outflow from the gulf in the surface layer (Kuzmić et al., 2006; Malačič and Petelin, 2009), and compensating intensified inflow at depth.

It has also been suggested that pre-bora ambient stratification plays a role in the response of the Northern Adriatic to bora (Jeffries and Lee, 2007). Typically, the water column in the GOT during the winter period is well mixed (Bogunović and Malačič, 2009; Celio et al., 2006). In April, surface heating and fresh water input lead to stratification and the months between May and September are characterized by strong density stratification (Malačič et al., 2006). In October, convective and mechanical mixing of the surface and subsurface

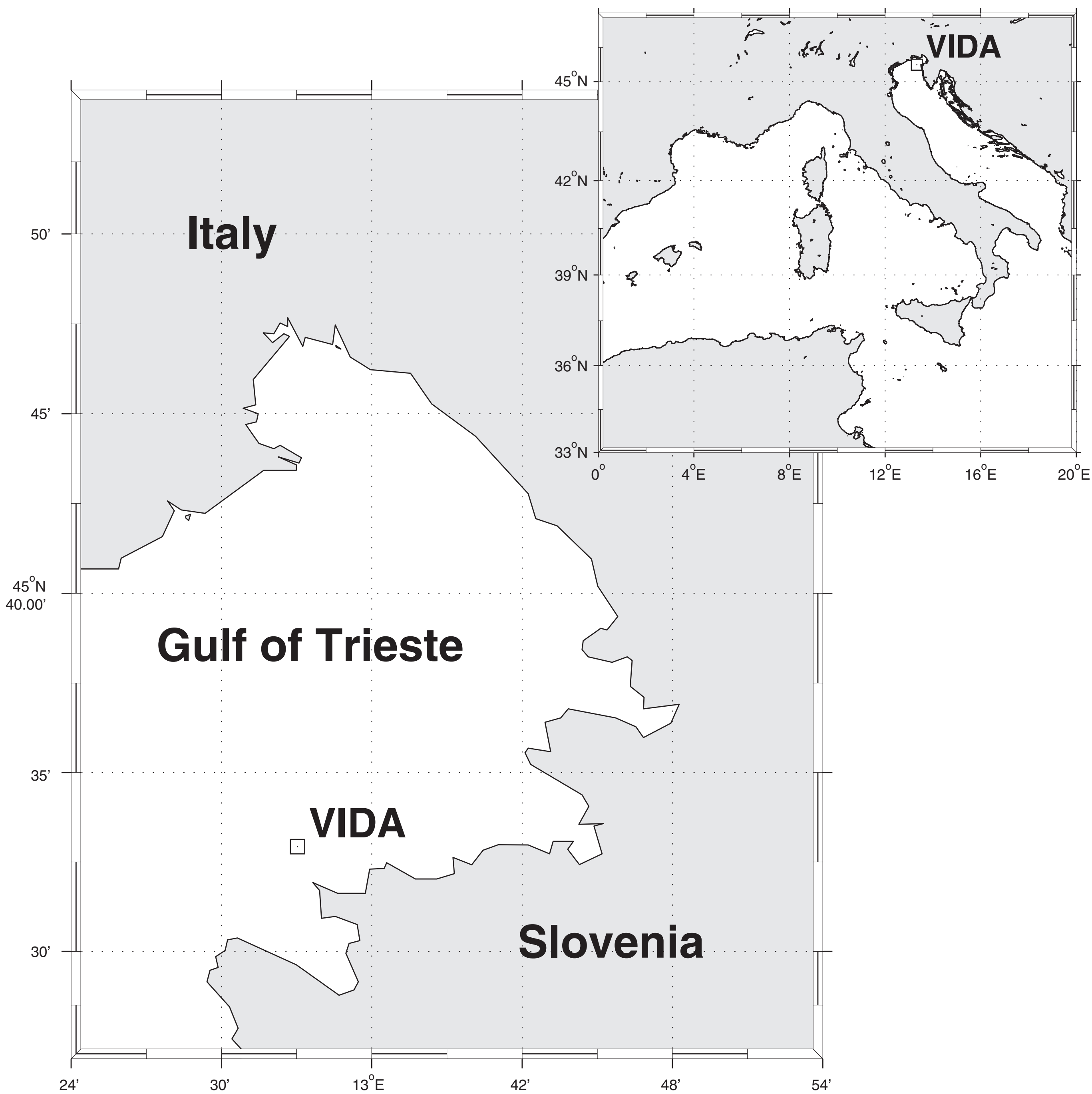

Fig. 1. Map of the (top) Mediterranean with the northern Adriatic Sea Gulf of Trieste and (bottom) GOT with location of the coastal oceanographic buoy Vida.

layers begin and mixing of the water column continues through November and December.

Despite the large number of studies on the physical oceanographic response to the bora wind in the Northern Adriatic, only a few observations are available on the biogeochemical responses (Boldrin et al., 2009; Cantoni et al., 2012; Turk et al., 2010). Boldrin et al. (2009) show the effect of the bora on dissolved nutrients and oxygen, suspended matter, and phytoplankton in the northern Adriatic during September 2002 with stratified conditions. Their observations indicate that the bora caused complete vertical mixing to 20–25 m in the water column, and an influx of warm salty water from the south along the Croatian coast. During bora conditions, they also observed an increase in resuspension of bottom sediment which is an important source of nutrients to the water column, and an increase in phytoplankton biomass. Turk et al. (2010) discuss a bora wind event in the Gulf of Trieste on October 30th–November 2nd, 2007 with winds reaching approximately 15 m s^{-1}, and sustaining 10–15 m s^{-1} for two days. They observed a sudden decrease of surface water pCO_2 by 25 μatm coinciding with the bora wind event. A possible reason for this could be that the pCO_2 decrease was due to a new water mass being advected to the measurement location. Cantoni et al. (2012) report enhanced air–sea CO_2 fluxes during bora events and measurable acidification (pH_T decrease) at station PALOMA in the central part of the Gulf of Trieste.

Here, we present three representative bora event cases during 2008 (Table 1); 21st–23rd July, 2008 (Case 1), 14th–16th November, 2008 (Case 2), and 25th–27th November, 2008 (Case 3) with the following objectives: 1) to describe the response of surface water pCO_2 and CO_2 fluxes during high bora wind events in the coastal Northern Adriatic and 2) to elucidate the relative importance of factors contributing to variation in pCO_2 and subsequent air–sea exchange. Specifically we consider the effect of temperature, vertical mixing, advection and air–sea gas exchange, while biological activity is not addressed due to lack of measurements and short time scale of events. We also examine the role of pre-bora ambient stratification in the response to bora by considering different pre-bora ambient conditions; (Case 1) stratified summer conditions with pCO_2 in the surface water above the atmospheric value, (Case 2) an autumn situation with a thermal inversion of bottom water temperature higher than sea-surface temperature (SST) and undersaturated water pCO_2, and (Case 3) a late autumn case when the temperature of the water column is nearly uniform and water pCO_2 is below the atmospheric value. All three bora cases are of 1.5–2 day duration with wind speeds exceeding 10 m s^{-1}.

2. Data and methods

Wind speed and direction, sea-surface temperature (SST) and sea-surface salinity (SSS), sea bottom temperature (T_b), and currents were all measured at the coastal buoy Vida located at 45° 32′ 55.68″ N, 13° 33′ 1.89″ E in the entrance of the GOT (Fig. 1). Surface water pCO_2 was measured with an autonomous sensor SAMI-CO_2 (Sunburst Sensors LLC) and wind speed was measured by a Gill 3D sonic anemometer at a height of 5 m. Currents were measured by a Nortek AWAC acoustic Doppler current profiler (ADCP) at one meter depth intervals situated on the sea bed beneath the buoy. Due to the surface echo contamination zone, the upper 4 bins of ADCP data were removed. Data from 3–4 additional bins at mid-depth were also removed as a result of contamination of the ADCP record, although the causes of this contamination could not be determined. This contamination does not affect the analysis of this paper. For SSS, a Seabird Seacat CT probe was used.

A measure of the thermal forcing on surface ocean pCO_2 (Takahashi et al., 2002) is determined as:

$$pCO_{2therm} = pCO_{2mean}\exp[0.0423(T_{obs} - T_{mean})] \quad (1)$$

Where T_{obs} are the observed SST values, and pCO_{2mean} and T_{mean} are the mean values of pCO2 (320 μatm) and SST (18.2 °C) as reported by Turk et al. (2010) during four deployments in 2007 and 2008 at the coastal oceanographic buoy Vida (Fig. 1). Air–sea CO_2 flux, F_{CO2}, (mmol m^{-2} day^{-1}) is estimated as:

$$F_{CO_2} = kS(pCO_2 - pCO_{2atm}) \quad (2)$$

where k (cm h^{-1}) is the gas transfer velocity and S (mol L^{-1} atm^{-1}) is the dissolved gas solubility in seawater at in situ temperature and salinity. We use the gas transfer velocity parameterization from Wanninkhof [1992], SAMI-CO_2 measurements of water pCO_2, and atmospheric pCO_2 values (pCO_{2atm}) derived from the atmospheric xCO_2 from the Lampedusa site in Italy (http://gaw.kishou.go.jp/wdcgg/wdcgg.html), SST and SSS from Vida and barometric pressure from the nearby weather station Portorož. The wind speed used to calculate the gas transfer velocity, U_{10}, was estimated using 30 min average measurements at 5.0 m on the buoy and adjusted to 10 m.

To estimate the general level of pCO_2 increase that could be attributed to gas exchange alone, we used gas fluxes as calculated above, mixed layer depths of half the water column (12 m) for Cases 1–2 and the full water column (25 m) depth for Case 3 (based on the observed velocity shears), the CO2SYS program of Lewis and Wallace (1998), measured values of SST, SSS, and pCO_2, and a constant total alkalinity (A_T) value from Cantoni et al. (2012).

3. Results

Three representative bora episodes during 2008 (Table 1) of 1.5–2 day duration with ENE wind speeds exceeding 10 m s^{-1}, acting on different pre-bora ambient conditions are described in more detail below.

Case 1 (21st–23rd July, 2008): Case 1 represents summer conditions when the water column prior to bora is stratified with SST higher than T_b by about 5 °C (Fig. 2a). pCO_2 in the surface water (Fig. 2b) is above the atmospheric value of 370.4 μatm reported at the Lampedusa site on 24th July, 2008. Early in the day of July 21st we observe the onset of ENE bora wind reaching speeds over 10 m s^{-1} (and up to 13 m s^{-1}) which persisted for 1.5 days (Fig. 2b). Shortly after the start of bora, pCO_2 and SSS increase by 40 μatm and 1 psu, respectively, and the

Table 1
Ambient pre-bora conditions and response during bora episode for three cases. Max refers to the maximum magnitude in columns 5–7.

Case no.	Date in 2008	Pre-bora water column conditions	Bora pCO_{2w} response	Mean ± SD and max U_{10} (m s^{-1})	Mean ± SD and max pCO_2–pCO_{2atm} (μatm)	Mean ± SD and max F_{CO2} (mmol m^{-2} d^{-1})	Likely responsible mechanism pCO_2 increase
1	21st–23rd July	Stratified (SST > T_b) pCO_{2atm} < pCO_2	Increase ~40 μatm	9.0 ± 2.8 13.3	38.4 ± 11.2 61.4	11.4 ± 7.6 29.0	Horizontal advection & vertical mixing
2	14th–16th November	Inversion (T_b > SST) pCO_{2atm} > pCO_2	Increase ~30 μatm	10.9 ± 1.8 14.5	−39.1 ± 7.1 −49.2	−12.6 ± 4.1 −22.6	Vertical mixing
3	25th–27th November	Non-stratified SST = T_b pCO_{2atm} > pCO_2	Increase ~50 μatm	10.0 ± 4.2 17.0	−37.1 ± 15.5 −61.3	−8.8 ± 6.8 −24.1	Horizontal advection

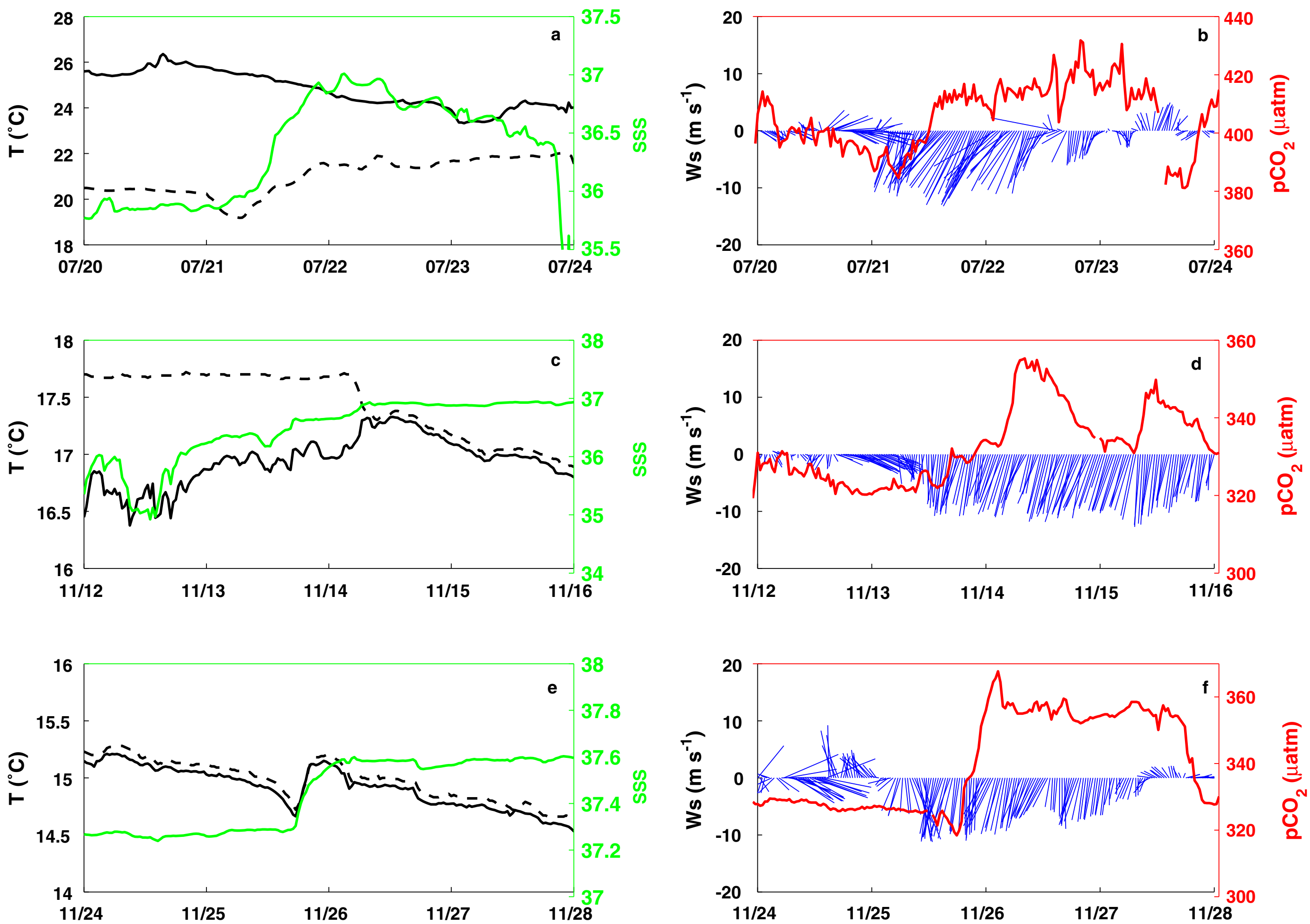

Fig. 2. (Left) SST (black solid), T_b (black dashed), and SSS (green), and (right) wind speed/direction (blue), and pCO_2 (red) during 21st–23rd July (Case 1—top panel), 12th–16th November (Case 2—middle panel), and 25th–27th November (Case 3—bottom panel), 2008.

difference between the SST and T_b decreases (Fig. 2a). pCO_{2therm} decreases over the event (not shown here) and as temperature decrease would lead to lower pCO_2, this indicates that the observed increase in pCO_2 was driven by changes in dissolved inorganic carbon (DIC) and A_T, and not by temperature changes.

The ocean current response at Vida to this bora event is complex (Fig. 3, top row). Several hours after the onset of strong winds, a strong bottom-layer alongshore (eastwards) inflow is established, followed shortly after by a strong upper-layer offshore (northward) flow directed slightly into the GOT (Fig. 3, top row). The latter flow is qualitatively in agreement with what would be expected from Ekman dynamics since the bora are upwelling favorable winds for the Slovenian coast and surface-layer Ekman transport near the coast should be directed to the right of the wind, toward the center of the GOT. However, this surface pulse of current is short-lived and while SSS and surface pCO_2 notably increase during this time, the surface temperature change is much less remarkable. After the upper-layer current pulse has stopped, the bottom-layer alongshore inflow continues with some modulation by the semidiurnal tide (Book et al., 2009; Malačič et al., 2000) and with a steadily decreasing thickness (Fig. 3, top row). This latter process is suggestive of vertical mixing as there is also a decrease in the temperature stratification observed at Vida (Fig. 2a).

Without measurements of the vertical and horizontal distribution of pCO_2 there is not enough data to firmly establish the source of the increased pCO_2 for this case. Likely, both surface horizontal advection and vertical mixing play a role. Horizontal advection could be responsible for the initial change, but waters coming from the bay south of Vida, after the initial upper-layer inflow pulse has stopped, are not expected to carry high SSS and high pCO_2. Upwelling could produce higher pCO_2 values but the temperature change of the surface waters is small and bottom waters are not directed onshore as might be expected from "classic" upwelling. Regardless, the later gradual increases in pCO_2 and SSS and the gradual decreases in stratification and bottom-layer thickness (Fig. 2ab) are all consistent with increased vertical mixing due to the continued action of the bora.

With increased U_{10} and air–water pCO_2 difference, the flux of CO_2 from the ocean into the atmosphere increases to a maximum of 29.0 mmol m^{-2} day^{-1}. The mean value over the event (21st–23rd July, 2008) was 11.4 ± 7.6 mmol m^{-2} day^{-1}. The direct effect of gas exchange alone should have decreased water pCO_2 by 2.3 μatm over the event.

Case 2 (14th–16th November, 2008): Prior to the onset of bora, our data show a thermal inversion with bottom temperatures higher than the SST by about 1.5–2 °C (Fig. 2c). A similar thermal structure in the fall was reported in the coastal GOT region by previous studies (e.g., Sept.–Oct. 2002 by Boldrin et al. (2009)). Surface waters are undersaturated with pCO_2 compared with the atmosphere (379.9 μatm at the Lampedusa site on 13th November, 2008). At mid-day on November 13th, the start of a bora with wind speeds over 10 m s^{-1} is observed and these winds persist for about 2 days (Fig. 2d). After about 14 h, the T_b decreases abruptly and the water column becomes mixed with a nearly homogeneous temperature (Fig. 2c). Coincident to this, we observe a sudden increase in pCO_2 by ~30 μatm (Fig. 2d), while salinity is

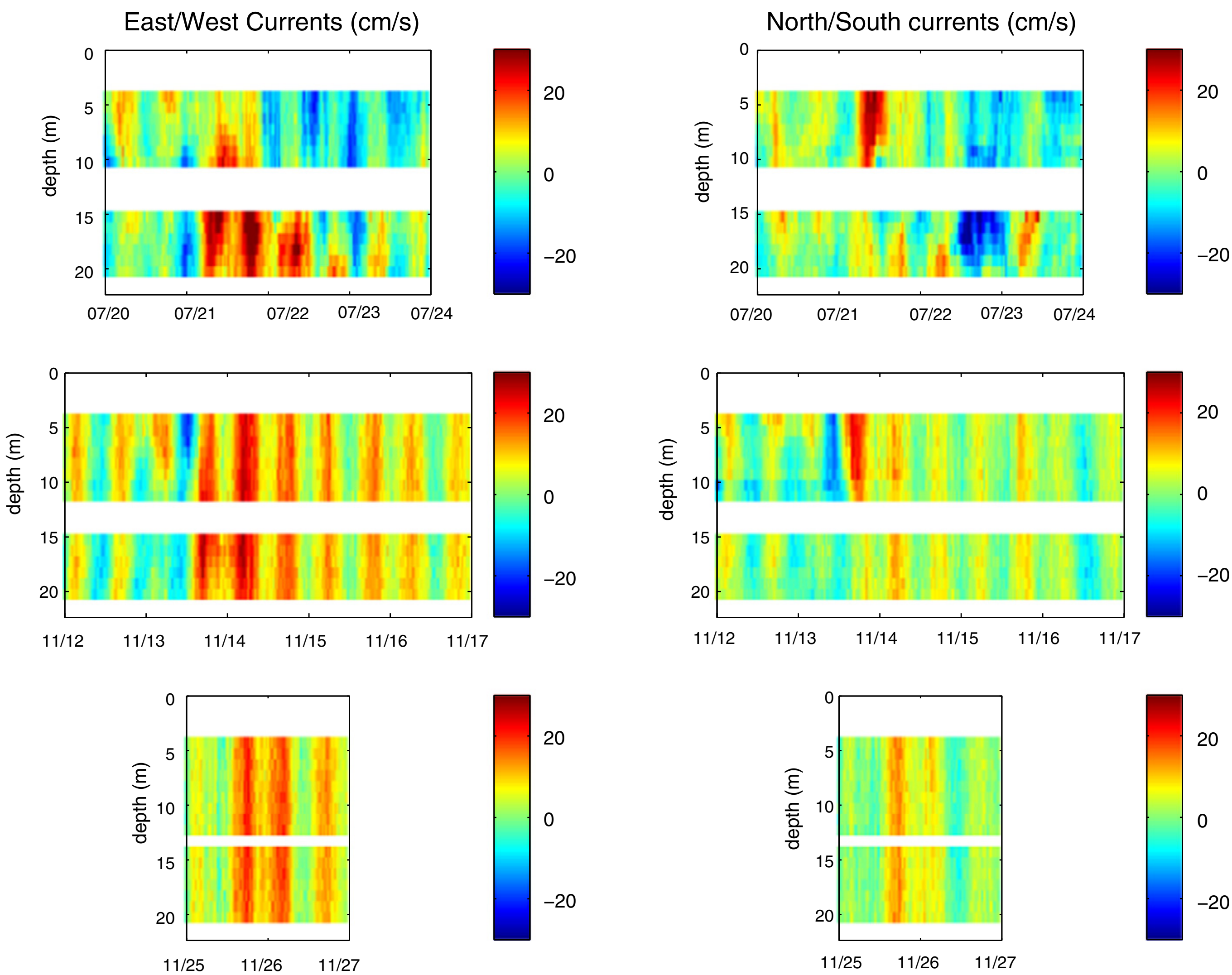

Fig. 3. (Left) East/west currents (cm s^{-1}) and (right) north/south currents (cm s^{-1}) at buoy Vida during 21st–23rd July (Case 1—top row), 12th–16th November (Case 2—middle row), and 25th–27th November (Case 3—bottom row), 2008.

only slightly elevated (Fig. 2c). pCO_{2therm} is nearly constant (not shown) and thus this increase in pCO_2 is not thermally forced.

These changes are strongly indicative of a bora enhanced vertical mixing process where warmer and saltier bottom water with higher pCO_2 suddenly mixes with colder and fresher surface water that has lower pCO_2. ADCP results (Fig. 3, middle row) support these findings as prior to the mixing event the surface flow is characterized by a strong anticyclonic oscillation absent from the bottom flow, but after the mixing event the flow becomes vertically uniform and directed alongshore (eastwards) in an inflowing direction (modulated by tides).

The air–sea CO_2 flux increases with the start of high wind and reaches up to a maximum of 22.6 mmol m^{-2} day^{-1}. However, when the undersaturation of pCO_2 decreases due to increases in surface water pCO_2, the flux is lowered. Mean flux over the bora episode, 14th–16th November, is -12.6 ± 4.1 mmol m^{-2} day^{-1} and should have increased water pCO_2 by about 3 µatm from gas exchange alone, representing 10% of the total observed increase of pCO_2 during the event (Table 1).

Case 3: (25th–27th November, 2008). Non-stratified conditions typical for late fall are observed (Fig. 2e) prior to the onset of bora and a weak NE to E current is present (Fig. 3, bottom row). Similarly as in Case 2, atmospheric pCO_2 value at the Lampendusa site on 27th November, 2008 (379.7 µatm) is higher than the surface waters. The onset of bora is observed early in the day on November 25th, reaching wind speeds over 10 m s^{-1} at about midday (Fig. 2f). After about 8 h of strong wind, sudden increases in pCO_2 (~50 µatm), SST and T_b (0.5 °C), and SSS are observed. pCO_{2therm} (not shown) remains almost constant and therefore the increase of pCO_2 is not temperature related.

ADCP data show vertically uniform currents bursting in an alongshore direction to the NE and E (Fig. 3, bottom row) similar to the latter portion of the current response to Case 2 (Fig. 3, middle row). This barotropic alongshore inflow to the GOT qualitatively agrees with Navy Coastal Ocean Model simulations of strong bora induced flow during 2003 winter (i.e. non-stratified) conditions (see Fig. 14 of Martin et al., 2006). Thus, water flowing past Vida is expected to have been transported from the south along the edge of a cyclonic gyre occupying the northernmost 60 km of the Adriatic. Satellite SST data (not shown) do indicate that waters to the south along the northern Istrian coastline are warmer than waters at Vida and some northward spreading of warmer waters during the bora is observed. The coincident change seen in SSS and pCO_2 suggests that these waters are also saltier and carry higher pCO_2 and therefore the increase in pCO_2 is mainly due to a horizontal advective flux. The change in SSS and pCO_2 is more sustained than the change in temperature

because further temperature changes are likely offset by bora cooling of the surface waters.

Similarly as in Case 2, the flux of CO_2 into the ocean initially increases drastically (up to 24.1 mmol m^{-2} day^{-1}) with the start of high wind, but drops to about 5 mmol m^{-2} day^{-1} when the increase of surface water pCO_2 decreases the level of undersaturation. Mean flux over the bora episode, 25th–27th November, is -8.8 ± 6.8 mmol m^{-2} day^{-1} and should have increased water pCO_2 by about 1 μatm from gas exchange alone, representing 2% of the total observed increase of pCO_2 during the event (Table 1).

4. Discussion

Our results (Table 1) show that CO_2 flux magnitudes during bora episodes peak up to 4 folds (22.6 mmol m^{-2} day^{-1} to 29 mmol m^{-2} day^{-1}) over the magnitude of the mean annual value of 6 mmol m^{-2} day^{-1} reported by Turk et al. (2010) and have magnitudes about 2 times greater than the annual mean magnitude when averaged over the duration of the bora events. Our average flux magnitude during the two winter events of -10.7 mmol m^{-2} day^{-1} is similar to values estimated by Cantoni et al. (2012) of -11.1 to -11.9 mmol m^{-2} day^{-1}. However, the time variability of pCO_2 measured during the storms in our 3 cases show that assumptions of single surface pCO_2 measurements being representative of whole wind events and that assumptions that wind mixing effects do not include horizontal water renewal are not generally true for bora in the Northern Adriatic.

In the summer time case, when surface waters were saturated with respect to the atmosphere, bora increased the CO_2 source potential of the GOT by increasing both (pCO_2–pCO_{2atm}) and transfer velocity. In the two winter cases, when surface waters were undersaturated, pCO_2 increased causing (pCO_2–pCO_{2atm}) to decrease in magnitude in Eq. (2), but the increase in k was more than enough to compensate for this, leading to an increase in F_{CO2} and enhancement of the ocean sink by the storm winds.

Supersaturated conditions in the summer persist only for about two months (Turk et al., 2010) and bora events are less frequent during the summer. With 40 days of bora per year and assuming that 10% occur over summer, this study implies that bora increases the flux from the atmosphere into the ocean on an annual time scale by 5%. As previous studies show that surface water pCO_2 can decrease during fall conditions (Turk et al., 2010) instead of increasing as is found for the cases considered here, the effect of bora wind events on CO_2 flux could possibly be larger for cases without decreasing delta pCO_2 through the event.

5. Conclusions

In all bora events studied here, pCO_2 increased in the surface water from pre-bora conditions, which is contrary to observations by Turk et al. (2010) that show a decrease in surface pCO_2 with the onset of bora. In the three cases studied here, pCO_{2therm} values show that the large variations in pCO_2 are not predominantly temperature controlled. In the two winter bora cases the amount of absorbed CO_2 into the ocean due to gas exchange was also too small to account for the increase in pCO_2. Gas exchange represented less than10% of the total pCO_2 increase, which is consistent with Cantoni et al. (2012) that report gas exchange led to changes in air–sea pCO_2 difference lower than 12%. In the summer case, gas exchange should decrease surface pCO_2 and therefore this mechanism certainly can't explain a pCO_2 increase. The SSS, temperature, and velocity data that were measured simultaneously to surface pCO_2 measurements all suggest that the most likely responsible mechanisms for the observed pCO_2 increases were vertical mixing and horizontal advection in varying degrees for the three cases.

In a shallow, semi-enclosed basin, such as the GOT, strong wind events can overcome stratification and efficiently mix bottom water pCO_2 with the surface water pCO_2. Winds, especially in shallow coastal environments, also play a strong role in moving different water masses, with different pCO_2 values, around through the local region. Both of these effects highlight the need to better understand and measure horizontal and vertical spatial gradients of oceanic pCO_2 when considering the impact of strong winds on CO_2 flux, as the magnitude (or direction) of air-sea pCO_2 difference can rapidly change through an event and drastically affect the flux.

Bora was present 11.6% (around 40 days per year) during 2007 and 2008 and we estimate that these winds increased the flux of CO_2 from the atmosphere into the ocean on an annual time scale by 5%. Our study contributes to a very limited set of observations currently available on the biogeochemical response to episodic high wind events in coastal areas and their role in CO_2 exchange.

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References

Bates, N.R., 2007. Interannual variability of the oceanic CO_2 sink in the subtropical gyre of the North Atlantic Ocean over the last 2 decades. J. Geophys. Res. 112, C09013. http://dx.doi.org/10.1029/2006JC003759.

Bates, N.R., Knap, A.H., Michaels, A.F., 1998. Contribution of hurricanes to local and global estimates of air–sea exchange of CO_2. Nature 395, 58–61.

Bogunović, B., Malačič, V., 2009. Circulation in the Gulf of Trieste: measurements and model results. Il Nuovo Cimento. http://dx.doi.org/10.1393/ncc/i2008-10310-9 (Online First).

Boldrin, A., Carniel, S., Giani, M., Marini, M., Bernardi Aubry, F., Campanelli, A., Grilli, F., Russo, A., 2009. Effects of bora wind on physical and biogeochemical properties of stratified waters in the northern Adriatic. J. Geophys. Res. 114, C08S92. http://dx.doi.org/10.1029/2008JC004837.

Book, J.W., Perkins, H., Wimbush, M., 2009. North Adriatic tides: observations, variational data assimilation modeling, and linear tide dynamics. Geofizika 26 (2), 115–143.

Cantoni, C., Luchetta, A., Celio, M., Cozzi, S., Raicich, F., Catalano, G., 2012. Carbonate system variability in the Gulf of Trieste (North Adriatic Sea). Estuarine Coastal Shelf Sci. 115. http://dx.doi.org/10.1016/j.ecss.2012.07.006.

Celio, M., Malačič, V., Bussani, A., Čermelj, B., Comici, C., Petelin, B., 2006. The coastal scale observing system component of ADRICOSM: Gulf of Trieste network. Acta Adriat. 47 (Suppl.), 65–79 (ISSN: 0001–5113 AADRAY).

Dorman, C.E., et al., 2006. February 2003 marine atmospheric conditions and the bora over the northern Adriatic. J. Geophys. Res. 111, C03S03. http://dx.doi.org/10.1029/2005JC003134 (printed 112 (C3), 2007).

Edson, J.B., et al., 2011. Direct covariance measurement of CO_2 gas transfer velocity during the 2008 Southern Ocean Gas Exchange Experiment: wind speed dependency. J. Geophys. Res. 116, C00F10. http://dx.doi.org/10.1029/2011JC007022.

Hood, E.M., Wanninkhof, R., Merlivat, L., 2001. Short timescale variations of CO_2 in a North Atlantic warm-core eddy: results from the Gas-Ex 98 carbon interface ocean atmosphere (CARIOCA) buoy data. J. Geophys. Res. 106 (2561–2572), 2001.

Jeffries, M.A., Lee, C.M., 2007. A climatology of the northern Adriatic Sea's response to bora and river forcing. J. Geophys. Res. 112, C03S02. http://dx.doi.org/10.1029/2006JC003664.

Kuzmić, M., Orlić, M., 1987. Wind inducing vertical shearing: Alpex/Metaplex data on modelling exercise. Ann. Geophys. Ser. B 5, 103–112.

Kuzmić, M., Janeković, I., Book, J.W., Martin, P.J., Doyle, J.D., 2006. Modeling the northern Adriatic double-gyre response to intense bora wind: A revisit. J. Geophys. Res. 111, C03S13. http://dx.doi.org/10.1029/2005JC003377 (printed 112(C3), 2007).

Lewis, E., Wallace, D.W.R., 1998. Program developed for CO_2 systems calculations. ORNL/CDIAC. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory, U.S. Department of Energy, p. 105.

Malačič, V., Petelin, B., 2006. Numerical modeling of the winter circulation of the Gulf of Trieste (northern Adriatic). Acta Adriat. 47 (Suppl.), 207–217.

Malačič, V., Petelin, B., 2009. Climatic circulation in the Gulf of Trieste (northern Adriatic). J. Geophys. Res. 114, C07002. http://dx.doi.org/10.1029/2008JC004904.

Malačič, V., Viezzoli, D., Cushman-Roisin, B., 2000. Tidal dynamics in the northern Adriatic Sea. J. Geophys. Res. 105, 26,265–26,280.

Malačič, V., Celio, M., Čermelj, B., Bussani, A., Comici, C., 2006. Interannual evolution of seasonal thermohaline properties in the Gulf of Trieste (northern Adriatic) 1991–2003. J. Geophys. Res. 111, C08009. http://dx.doi.org/10.1029/2005JC003267.

Martin, P.J., Book, J.W., Doyle, J.D., 2006. Simulation of the northern Adriatic circulation during winter 2003. J. Geophys. Res. 111, C03S12. http://dx.doi.org/10.1029/2006JC003511 (printed 112(C3), 2007).

Pullen, J., Doyle, J., Haack, T., Dorman, C., Signell, R., Lee, C., 2007. Bora event variability and the role of air–sea feedback. J. Geophys. Res. 112, C03S18. http://dx.doi.org/10.1029/2006JC003726.

Signell, R.P., Chiggiato, J., Horstmann, J., Doyle, J.D., Pullen, J., Askari, F., 2010. High-resolution mapping of Bora winds in the northern Adriatic Sea using synthetic aperture radar. J. Geophys. Res. 115, C04020. http://dx.doi.org/10.1029/2009JC005524.

Stravisi, F., 2001. La Bora a Trieste (The bora wind in Trieste). Unione Meteorologica Friuli-Venezia Giulia, Atti I Conv, pp. 23–34.

Takahashi, T., Sutherland, S.C., Sweeney, C., Poisson, A., Metzl, N., Tilbrook, B., Bates, N., Wanninkhof, R., Feely, R.A., Sabine, C., Olafssong, J., Nojiri, Y., 2002. Global sea air CO_2 flux based on climatological surface ocean pCO_2, and seasonal biological and temperature effects. Deep Sea Res. Part II 49, 1601–1622. http://dx.doi.org/10.1016/S0967-0645(02) 00003-6.

Turk, D., Malačič, V., DeGrandpre, M.D., McGillis, W.R., 2010. Carbon dioxide variability and air–sea fluxes in the northern Adriatic Sea. J. Geophys. Res. 115, C10043. http://dx.doi.org/10.1029/2009JC006034.

Zavatarelli, M., Pinardi, N., 2003. The Adriatic Sea modeling system: a nested approach. Ann. Geophys. 21 (Part 2), 345–364.